

A NEW APPROACH TO THE CALORIMETRIC INVESTIGATION OF PHYSICAL AND CHEMICAL TRANSITIONS

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The theoretical basis for Modulated DSC is described and the additional information it can give over conventional DSC illustrated for some polymers.

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Introduction

Differential scanning calorimetry (DSC) has been used for over twenty years to characterise physical transformations such as melting and glass transitions as well as chemical reactions such as epoxy-amine cross-linking in thermoset polymers. In its most common form, called heat flux DSC, this technique consists of measuring the temperature difference between a sample and a reference while the temperature of the environment in which they both sit is increased linearly with time. This temperature difference is related to the difference in heat flow into the sample compared to the usually inert reference material. This simple system can be used to measure properties such as heat capacities, melting temperatures, heats of melting, reaction kinetics etc. Here we show how by modulating the temperature ramp with a sinusoidal ripple the amount of information that can be obtained from this type of experiment can be substantially increased. This new technique is called Modulated DSC or MDSC.

Theory

The normal response of a DSC is a combination of a signal that is dependent on the rate of change of temperature and one that is dependent on the absolute

value of the temperature as this will govern the rate of any kinetically driven process viz;

$$dQ/dt = C_p \cdot dT/dt + f(t, T) \quad (1)$$

where Q = amount of heat evolved

C_p = heat capacity

T = absolute temperature

t = time

$f(t, T)$ = some function of time and temperature that governs the kinetic response of any physical or chemical transformation

In the case of MDSC the temperature programme is given by

$$T = bt + B \cdot \sin(\omega t) \quad (2)$$

where ω = frequency

b = heating rate

B = amplitude of temperature excursion

If we assume that the temperature excursions are small and that over this interval the response of the rate of the kinetic process to temperature can be approximated as linear, we can rewrite Eq. (1) as

$$dQ/dt = C_p (b + B\omega \cdot \cos(\omega t)) + f'(t, T) + C \cdot \sin(\omega t) \quad (3)$$

where $f'(t, T)$ = the underlying kinetic function once the effect of the sine wave modulation has been subtracted

C = amplitude of kinetic response to the sine wave modulation

$(b + B\omega \cdot \cos(\omega t))$ = the measured quantity dT/dt

It can be seen that the heat flow signal will contain a cyclic component that will depend on the value of B , ω and C .

Experimental

Figure 1 shows a normal DSC response for a sample of quenched polyethylene terephthalate (PET). A glass transition (T_g), a recrystallisation exotherm and a melting endotherm can be observed. Figure 2 shows the results for the same type of sample using MDSC. Though the response is considerably changed, the three transitions can still be seen. The two basic measurements are dQ/dt and the phase angle lag which is the difference between the cosine wave generated in the dT/dt signal and the cyclic component found in the dQ/dt response. There is an offset in the baseline of the phase lag due to the masses of the sample and reference crucibles, the quality of thermal contact between the

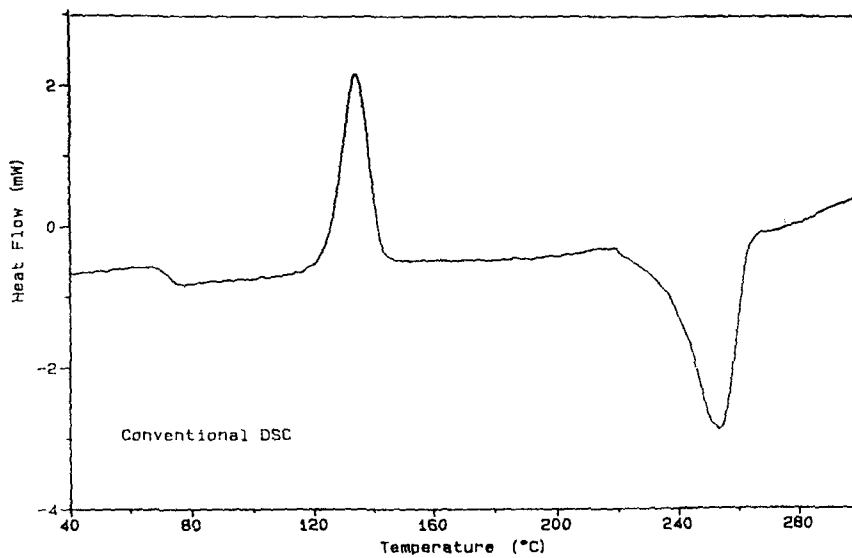


Fig. 1 Conventional DSC result for quenched polyethylene terephthalate

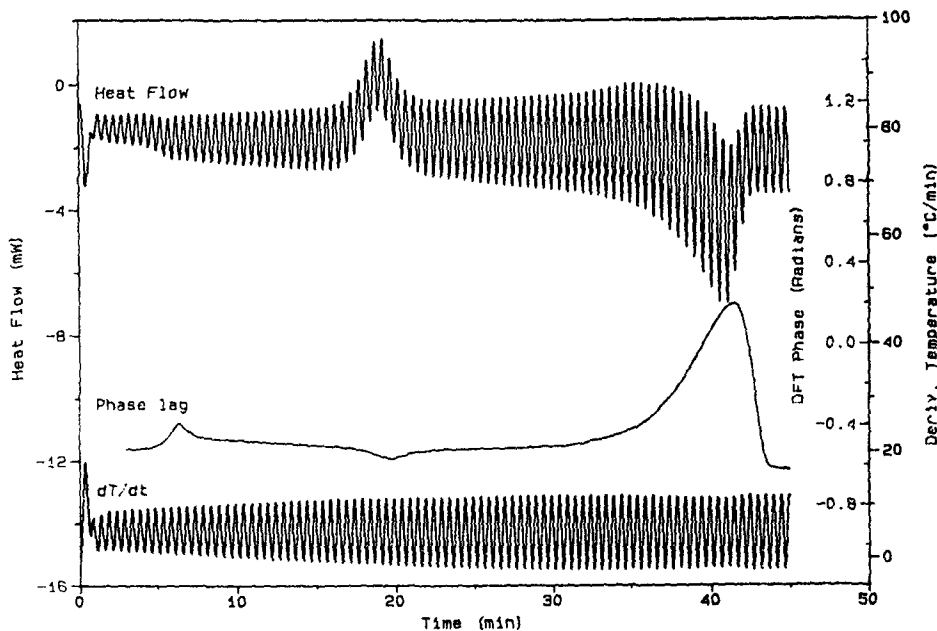


Fig. 2 Modulated DSC result for quenched polyethylene terephthalate illustrating heat flow, phase lag and dT/dt signals

crucibles and the floor of the cell, and the thermal resistance between the sample and the measuring thermocouple.

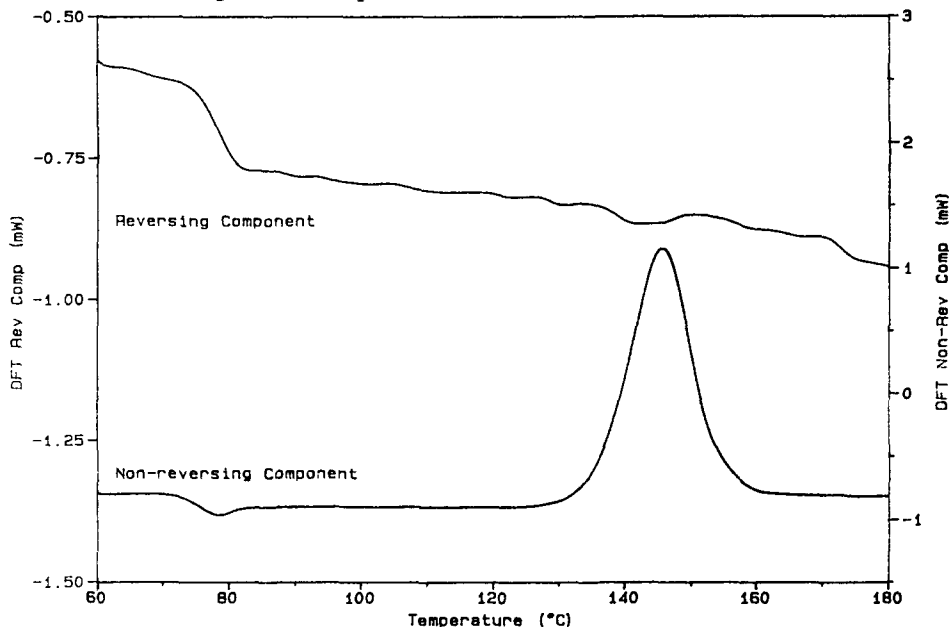


Fig. 3 Deconvoluted reversing and non-reversing signals for the glass transition and the recrystallisation peak for PET

A contribution from the sine component in Eq. (3) can only occur when there is an enthalpic event such as an exotherm from a recrystallisation or cure reaction or an endotherm arising from a melting or a relaxation event. The cosine wave contribution is always present and is, in this case, by far the major part of the cyclic component in the heat flow signal for all of the transitions except melting. This is confirmed by the small peaks in the phase lag seen at the T_g and recrystallisation. When this occurs, C can be taken as zero and a simple deconvolution procedure applied. Using a Discrete Fourier Transform (DFT) algorithm the cyclic component is subtracted from the signal effectively reconstituting the underlying signal i.e. the result a traditional DSC would have given. We refer to this output as the total heat flow. These curves are virtually indistinguishable from traditional DSC results obtained at the same underlying heating rate. The same DFT procedure is applied to both the dT/dt and temperature signals thus giving the 'underlying' heating rate and temperature at any point in time. The amplitude of the cyclic component of the dT/dt signal can be compared with the cyclic component from the dQ/dt signal, thus enabling a value for C_p to be deter-

mined. The contribution to the reconstituted total heat flow that arises from the heat capacity can then be calculated by multiplying C_p by the value for the underlying heating rate. This is referred to as the reversing component as this response changes in an effectively instantaneously reversible fashion. When this is subtracted from the reconstituted total heat flow the non-reversing component is obtained as illustrated in Fig. 3. It can now be seen that the glass transition occurs only in the reversing component while the enthalpic relaxation that occurs during this transition and the subsequent recrystallisation are seen only in the non-reversing component. This is intuitively what one would expect and some immediate practical benefits accrue from this.

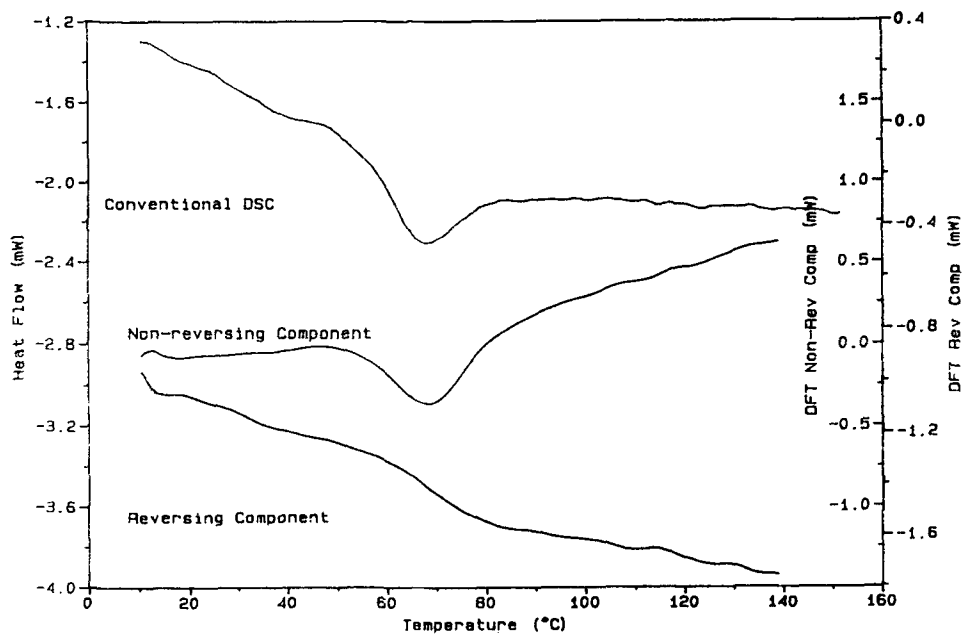


Fig. 4 Conventional DSC and MDSC results showing how a relaxation peak can be separated from a glass transition

Some relaxation events that accompany glass transitions are so energetic that the glass transition is obscured. Figure 4 shows a transition of this type. With conventional DSC the result could be misinterpreted as being purely an endotherm due to melting or the loss of volatile material. The MDSC results unambiguously show the true nature of this type of event. A clear glass transition is seen in the reversing signal with the endotherm confined to the non-reversing component.

Overlapping transitions such as recrystallisations and T_g can also be successfully separated. This is of considerable benefit when characterising complex mixtures and composite materials. Figure 5 shows the results for a mixture of

polyethylene terephthalate and polycarbonate. The standard DSC curve shows one T_g and a recrystallisation peak. By separating the reversing and non-reversing components it can be seen that another T_g had been masked by the recrystallisation exotherm.

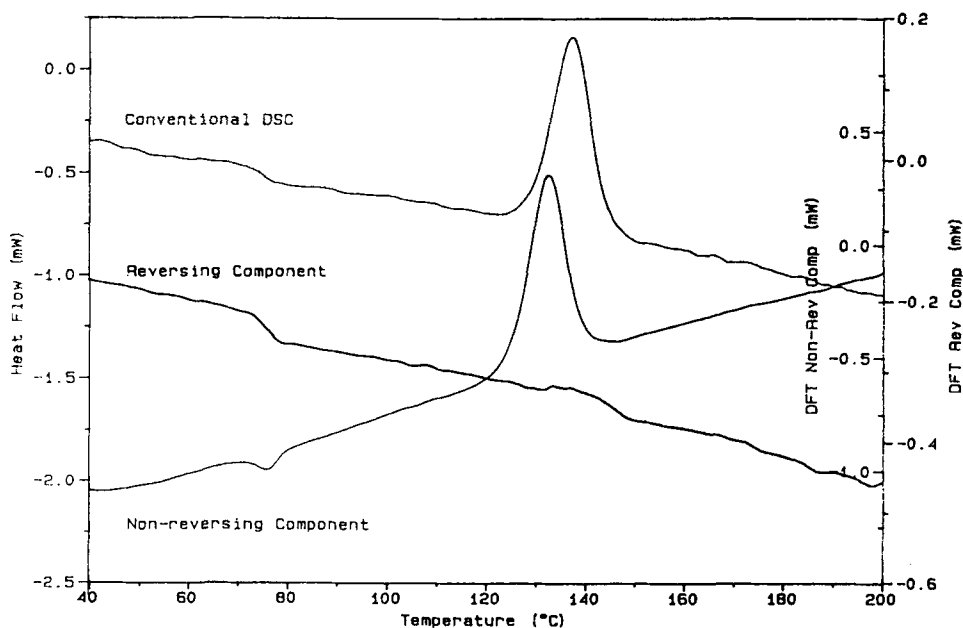


Fig. 5 Conventional DSC and MDSC results showing how a glass transition can be separated from a recrystallisation peak

A further benefit is that heat capacity and consequently glass transitions can be reliably measured at low underlying heating rates. High heating rates are normally required to discern glass transitions where only a small change in C_p occurs, as the strength of the signal generated by these events is proportional to the heating rate. This inevitably reduces resolution not only for the glass transition but also for other enthalpic events that occur during the experiment. MDSC effectively eliminates this problem making it possible to conduct experiments at $1 \text{ deg}\cdot\text{min}^{-1}$ or even less.

Results given by this method are even more interesting when the melting peak is considered. The large sine wave contribution makes a further deconvolution stage necessary to distribute the cyclic component of the heat flow signal between C_p and C , i.e. between components that are in-phase with the dT/dt signal or in-phase with the modulation of the absolute temperature respectively.

Conclusions

Using MDSC we have already found interesting effects in polymorphic behaviour of pharmaceuticals, the melting behaviour of oriented polymers and the heat capacity of inorganic solids that would not be observable with conventional DSC or any other method known to us. The development of theoretical models to enable full quantitative interpretation of many of our results is in progress and qualitative insights are already emerging.

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Zusammenfassung — Es werden die theoretischen Grundlagen für modulierte DSC sowie diejenigen zusätzlichen Informationen beschrieben, die man in Vergleich zu üblicher DSC erhalten kann, was anhand einiger Polymere veranschaulicht wird.